

REACTIONS OF MUSTARD ON CONCRETE

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ABSTRACT

The reactions of the blister agent mustard, (bis(2-chloroethyl) sulfide, HD), and chloroethyl phenyl sulfide, CEPS*,¹ a simulant, were monitored on concrete, asphalt and sand substrates. The CDCl_3 extract of concrete monoliths was analyzed using both NMR and GC/MSD; the percent HD extracted depended upon its contact time with the concrete before extraction. Vinyl, hydroxyl, sulfoxide, and dimerized products were detected. ^{13}C SSMAS NMR measurements of CEPS* on the concrete, asphalt and sand substrates indicated a strong interaction between the CEPS* and asphalt and one type of concrete; all of the other interactions were weak. The CEPS* that was placed on the CZ2000 concrete reacted over a period of four weeks to form hydrolysis and dimerized products; no reaction was detected on the sand, TinkerB, or ACE substrates over this period of time.

1. INTRODUCTION

Knowledge of when a CWA (Chemical Warfare Agent) no longer poses a threat – that is, when a contaminated area is safe to enter without protective clothing – is of major concern for battlefield commanders. Decisions must be made whether to decontaminate an area, or if natural weathering alone will allow resumption of normal operations after an acceptable waiting period.

Mustard (bis(2-chloroethyl) sulfide, has previously been shown to persist for four years on soil. It hydrolyzed and polymerized to form toxic CH-TG² and H-2TG³ over this period of time.⁴ Prior studies of the extraction of mustard from concrete using isopropanol or acetonitrile and GC/MS analysis of the solvent showed 0 to 67% recovery of mustard (personal communication from R. McGuire).

In the current study, extraction and in situ NMR techniques were applied to investigate the persistence and reactivity of HD and CEPS* on Asphalt, three types of concrete, and their component sand and limestone materials.

2. EXPERIMENTAL

2.1 Substrates

The Asphalt sample, sand, and one concrete sample (CZ2000) were obtained from the Czech Republic. The Limestone and other two concrete samples (ACE and TinkerB) were obtained from the Army Corps of Engineers. The ACE and TinkerB were runway concrete formulations made with limestone filler; the ACE was made with low-iron cement, and the TinkerB was obtained from a core sample of a used runway. The CZ2000 concrete was made using silica filler.

2.2 Extraction of HD from Concrete

Four 1 μL drops of CASARM (Chemical Agent Standard Analytical Reference Material) grade HD ($\text{ClCH}_2\text{CH}_2\text{S}_2$) were placed onto 5 mm x 9 mm x 15 mm monoliths of CZ2000 concrete. After exposure times of 1, 8, and 24 hours, the samples were extracted with 4 mL CDCl_3 , crushed, and re-extracted with 2 mL CDCl_3 . The extract was analyzed using GC/MSD, and liquids ^{13}C and ^1H NMR. Two-dimensional ^1H - ^{13}C and ^1H - ^1H NMR studies of the extract (made with ^{13}C -labeled HD) were used to identify products.

2.3 Solid State Magic Angle Spinning (SSMAS) NMR of CEPS* on Substrates

Each substrate was ground into a fine powder and packed into a 5 mm diameter x ~10 mm length sample area of a solid state rotor. One 4 to 8 μL drop of CEPS* ($\text{ClC}^*\text{H}_2\text{C}^*\text{H}_2\text{SPh}$) was injected onto the powder, and the sample was capped. The samples were spun at ~2000 Hz in a 400 MHz Varian Inova NMR instrument.

3. RESULTS AND DISCUSSION

3.1 Extraction of HD from CZ2000

The percentage of HD recovered decreased as the contact time increased. It was determined that removal of the HD from the one-hour contact time samples was quantitative after two extractions; thus, the same protocol was followed for all samples. The GC/MSD and NMR techniques showed the same trend for the total amount of material extracted, although the GC generally gave higher percent recoveries than the NMR technique did.

¹ The * indicates that the compound is ^{13}C labeled.

² CH-TG is $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{Cl}^-$

³ H-2TG is $\text{S}(\text{CH}_2\text{CH}_2\text{S}^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{Cl})_2$

⁴ Wagner, G. W. and MacIver, B. K. 1998: Degradation and Fate of Mustard in Soil as Determined by ^{13}C MAS NMR, *Langmuir*, **14**, 6930-6934.

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Eight different products were found by using the two detection techniques. 2-chloroethyl vinyl sulfide was found by both techniques; the other products differed. It was often difficult to detect thiodiglycol using the GC/MSD technique, and thus it was only identified in the NMR. Many of the compounds observed in the GC were not detected in the NMR. This is likely due to the amount of compound present; a more concentrated solution and/or longer NMR acquisition times would probably reveal these compounds.

The products show that hydrolysis of the Cl, oxidation of the S, and reduction of the ethyl group all occur. In addition, these species dimerized to form other compounds, such as Q.

Table 1. Percent HD Extracted from CZ2000 Concrete based on NMR Data

Hours	First Extract		Second Extract		% Total
	% HD	% Products	% HD	% Products	
1	75.3	0.0	26.0	0.0	101.3
8	58.0	0.0	9.0	0.0	67.0
24	18.7	2.0	27.7	2.4	50.8

Table 2. Products Found in Extracts of CZ2000 after 24-hour Exposure to HD

Both Techniques
2-chloroethyl vinyl sulfide, $\text{CH}_2=\text{CHSCH}_2\text{CH}_2\text{Cl}$
Bis(2-chloroethyl) sulfoxide, $\text{ClCH}_2\text{CH}_2\text{SOCH}_2\text{CH}_2\text{Cl}$
NMR
Thiodiglycol, $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$ (TDG)
GC/MSD
2-hydroxyethyl vinyl sulfide, $\text{CH}_2=\text{CHSCH}_2\text{CH}_2\text{OH}$
2-chloroethyl-2-hydroxyethyl sulfide, $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$
Q, $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$
HD-disulfide, $\text{ClCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{Cl}$

3.2 CEPS* on Crushed Substrates

The Asphalt and CZ2000 substrates exhibited very strong spinning side bands; the main peaks accounted for only ~50% of the overall total integrated peak areas. Strong spinning side bands are generally indicative of a high degree of order in the substrate; in this case the interpretation is that the strong spinning side bands imply strong binding between the CEPS* and the substrate. A further implication is that the materials that have weak spinning side bands will have a higher vapor hazard; this needs to be verified by an independent technique.

The samples were monitored over a period of four weeks. Only the CEPS* on ACE sample showed any reaction; it produced the hydroxyl product, ($\text{HOCH}_2\text{CH}_2\text{SPh}$) and another species that is tentatively identified as its ether, $\text{O}(\text{CH}_2\text{CH}_2\text{SPh})_2$.

Table 3. Percentage Total Integrated Peak Area in Main Peaks for CEPS* on Various Substrates

Crushed Substrate	% Intensity in Main Peaks
CZ2000	50
Asphalt	58
TinkerB	75
Limestone	85
ACE	95
Sand	99

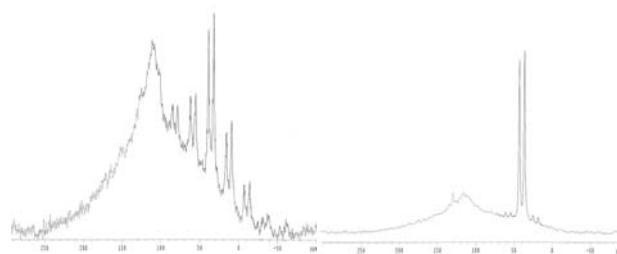


Figure 1. ^{13}C NMR SSMAS spectrum of CEPS* on a) crushed CZ2000 concrete and b) sand.

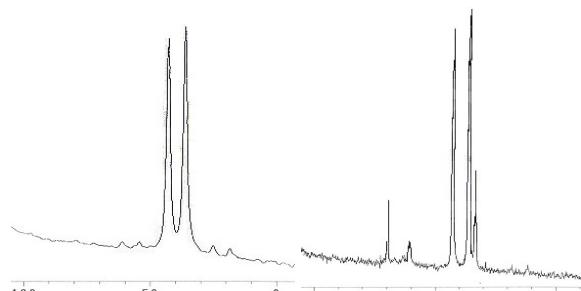


Figure 2. Initial and 4-week ^{13}C SSMAS spectra of CEPS* on ACE concrete.

CONCLUSIONS

Mustard ($\text{ClCH}_2\text{CH}_2\text{S}$) that was placed onto ambient concrete samples formed vinyl, hydroxyl, S-oxidized and dimerized species after a period of 24 hours.

The use of NMR allowed for the identification of non-volatile and non-extractable species within a solid matrix.

Concrete from various sources exhibited different reactivity towards the CEPS*. Over a four-week period of time products were observed on the ACE concrete, but not on the other substrates.

Future studies will focus on the variability of mustard decomposition on different types of concrete.